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Scanning Probe Lithography. 2. Selective Chemical Vapor Deposition of Copper into Scanning
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by
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Abstract

A scanning tunneling microscope (STM) has been used to define features having critical dimensions ranging from 0.05 to 5.0 μm within a self-assembled monolayer resist of octadecylmercaptan, $HS(CH_2)_{17}CH_3$, confined to a Au (111) surface. Low temperature chemical vapor deposition (CVD) methods were used to metalize the STM-patterned surface with Cu. At substrate temperatures near 120 °C, the Cu CVD precursor, hexafluoroacetylacetonatocopper(I)-(1,5-cyclooctadiene), disproportionates to deposit Cu on the STM-etched portion of the substrate, but not on the unetched methyl-terminated monolayer resist surface. At substrate temperatures significantly above 120 °C the degree of selectivity is reduced, probably as a result of thermal desorption of the organomercaptan monolayer.

We report a two-step lithographic process that is based on scanning probe microscope-induced lithography and selective low-temperature chemical vapor deposition (CVD) metalization. We use the tip of a scanning tunneling microscope (STM) to pattern a high-density resist[1] that is composed of a single, self-assembled n-alkanethiol monolayer a few nanometers thick.[2-4] Lithography is followed by low-temperature Cu CVD, which is based on the disproportionation reaction of hexafluoroacetylacetonatocopper(I)-(1,5-cyclooctadiene), (hfac)Cu(1,5-COD),[5-11] to selectively metalize the exposed pattern (Scheme I).[5,9,12] This treatment

Scheme I

results in geometrically well-defined micron- and submicron-scale Cu features. Our new results are significant for four reasons. First, the resist is only a single monolayer thick, yet under the proper conditions it passivates the underlying substrate towards CVD metalization. Second, the resist is molecular and well-ordered, and therefore the ultimate lithographic resolution should be controlled only by the lateral dimensions of a single resist molecule (< 1 nm). Third, the thermal constraints of the CVD chemistry are compatible with the lability of the resist. Fourth, by analogy to bulk-phase deposition, the vapor-deposited metal features should be of very high purity.[5,9]

Prior to this report, high-energy electron- and ion-beam methods, as well as x-ray and deep-UV photolithographic methods, have been used to define submicron-scale features in polymeric

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resists. For example, electron-beam technology has been combined with physical vapor deposition methods to yield features that have critical lateral dimensions in the range 20 - 100 nm.[13-15] However, this approach has inherent limitations, which include proximity effects and electron scattering, that appear to preclude further resolution enhancement. Scanning probe microscope (SPM)-induced lithography is an alternative to more traditional approaches, since the resolution limits associated with high-energy beam methods are avoided. For example, lithographic methods based on STM and scanning force microscopy (SFM) have recently been used to directly modify substrates either in the presence[16-22] or absence[23-34] of active chemical reactants or etchants. SPM-based lithographic methods have also been used to define features in polymeric resists.[35-39] In a few cases such features were subjected to metalization and lift off.

To insure that the CVD precursor used in the experiments reported here would selectively deposit on the exposed Au surface, but not on the methyl-terminated resist surface, and to insure that the thermal requirements of the CVD chemistry would be compatible with the resists, we performed the following control experiment. We examined the relative degree of selectivity for Cu deposition from the (hfac)Cu(1,5-COD) precursor onto macroscopic naked and $HS(CH_2)_{17}CH_3$-coated Au surfaces as a function of substrate temperature. We previously showed that (hfac)Cu(1,5-COD) disproportionates and selectively deposits high-purity Cu on metals in the temperature range 120-200 °C, but not on alkylsiloxane-coated SiO_2 surfaces.[40,41] Since ultrahigh vacuum

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temperature programmed desorption experiments have shown that $HS(CH_2)_{15}CH_3$ monolayers confined to Au(111) surfaces begin to desorb near 225 °C, we anticipated that the resists and the CVD chemistry would be compatible.[42]

The substrates used for these macroscopic selectivity experiments were Au-coated Si(100) wafers. Both naked Au substrates and Au substrates coated with the monolayer resist were subjected to the CVD process. The resist-coated substrates were prepared by immersion of the nominally clean Au surface in an ethanolic 0.5 mM $HS(CH_2)_{17}CH_3$ solution. Chemical vapor deposition was performed at substrate temperatures between 120 and 200 °C with the precursor in the temperature range 75-88 °C. Details of the CVD process have been described elsewhere.[5,9]

Chemical vapor deposition onto the naked Au substrates held at 120 °C or above for 15 min yields uniform Cu coatings, which is consistent with our previous reports,[5,9] ranging in thickness from about 0.3 to 0.5 μm depending on the deposition temperature. X-ray diffraction data indicate that the films are oriented Cu(111). Monolayer-coated substrates held at 120 °C for 15 min were sparsely coated with submicron Cu nuclei (2.5×10^3 nuclei/mm^2). When we reduced the deposition time to 3.5 min, however, all nucleation was eliminated on the coated substrates within the resolution of SEM. Above 140 °C, all selectivity was lost within 10 min of exposure of the monolayer-coated substrate to the Cu CVD precursor, and the surfaces were densely perforated with Cu nucleation sites (8.9×10^5 nuclei/mm^2). When we heated a monolayer-coated substrate to 140 °C for 15 min in the presence of

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only pure N_2, and then cooled it to 120 °C prior to a 6 min (hfac)Cu(1,5-COD) exposure, we found that the resulting surface again consisted of densely distributed Cu nucleation sites. In contrast, essentially no Cu was found on a monolayer-coated substrate that was not heated to 140 °C, but otherwise treated identically. On the basis of these experiments we conclude that the methyl-terminated surface virtually eliminates (hfac)Cu(1,5-COD) disproportionation and substrate metalization for exposure times less than 3.5 min at 120 °C. Above 120 °C, the monolayer undergoes partial desorption, a process which may be assisted by (hfac)Cu(1,5-COD); below 120 °C Cu deposition from (hfac)Cu(1,5-COD) does not proceed on either the coated or uncoated Au substrates.

For the STM lithography/metalization experiments, we used a resist consisting of a single monolayer of $HS(CH_2)_{17}CH_3$ self-assembled onto a Au(111) surface.[1] The substrates were prepared by melting a 0.25-mm diameter Au wire (Johnson-Matthey, 99.998%) in a H_2/O_2 flame under N_2, and then annealing in a cooler region of the flame.[1,43] This treatment results in approximately 1.0 mm-diameter spheres that contain a few Au (111) facets on the surface. The facets are typically elliptical, with a long axis of 200-300 μm, and are composed of atomically flat terraces 200-1000 nm wide. Prior to monolayer adsorption, the Au balls were electrochemically cleaned in an aqueous 0.1 M $HClO_4$ solution to reduce the amount of adventitious surface adsorbates. The freshly prepared surface was immersed in a 0.5 or 1.0 mM ethanolic solution of $HS(CH_2)_{17}CH_3$ for

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18-24 h, removed, rinsed with ethanol, and then attached to a home-built STM-substrate holder for subsequent STM-lithography.[1]

We have previously shown that features with critical dimensions ranging from 0.025 μm to more than 10 μm can be directly written into $HS(CH_2)_{17}CH_3$ resists using the tip of an appropriately biased STM.[1] In this study, we used a NanoScope III STM (Digital Instruments, Inc.) to define patterns with critical dimensions ranging from 0.05 to 5.0 μm. There are several possible tip/substrate interactions that could lead to resist removal. These include: (a) electron-beam-induced degradation or desorption (for example, field-induced electron emission); (b) field ionization of molecules near the tip/substrate gap; (c) physical abrasion; (d) Joule heating of the substrate. Since very little is known about the physical and chemical conditions present between the STM tip and the substrate, particularly when the STM is operated in air, it is premature to speculate about the mechanism or combination of mechanisms responsible for STM patterning in this report.[1]

Figure 1 shows scanning electron micrographs of STM-

Figure 1

patterned monolayer surfaces before and after Cu deposition. In Figure 1a, 5 square patterns are present that have sides of (nominally) 0.1, 0.5, 1.0, 2.0, and 5.0 μm. The 0.1 μm feature is not clearly resolved at this magnification, but it is located just below the 1.0 μm feature. All of these patterns were

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lithographically defined by scanning the surface 4 times at high

tip bias followed by 4 additional scans at low bias; the specific

conditions used for patterning are given in the figure captions.

We also obtained STM images of features like those shown in Figure

1a, but they are usually of poor quality since the etching process

damages the tip.[44] STM line scans through the etched regions

usually indicate resist walls that are between 0.7 and 0.9 nm

high. The dark particulate matter, which is primarily distributed

parallel to the slow-scan axes of the images, is either organic

resist material or Au from the substrate that is removed during

patterning.[1]

Following STM patterning, substrates were transferred to the

hot-wall CVD apparatus[5] and then exposed to (hfac)Cu(1,5-COD).

Figure 1b shows a scanning electron micrograph of an STM-patterned

Au surface after exposure to (hfac)Cu(1,5-COD) for 3.5 min at 120

°C.[44] Cu has deposited into all of the square patterns, 3

rectangular features, and along two lines connecting the 0.5, 1.0,

and 2.0 μm Cu squares. We also observe Cu deposits that are

coincident with the debris present along the edges of the

patterns. From these data, we infer that this material, which may

be resist or Au, serves as suitable sites for Cu deposition. We

also obtained energy dispersive spectroscopic data in and near the

metalized features shown in Figure 1b. These data clearly

indicate the presence of Cu only in the patterned regions. By

analogy to the product of (hfac)Cu(1,5-COD) decomposition on

macroscopic, naked Au surfaces we infer that the Cu deposits are

of high purity, but at the present time direct confirmation of

this conclusion, especially in the smallest patterns, is a difficult analytical problem.

Figure 2 shows two Cu features at higher magnification.

Figure 2

Figure 2a shows one of the Cu wires, which was formed by scanning the STM tip once between the 0.5 and 1.0 µm square features shown in Figure 1b. The formation of a continuous Cu wire is interesting, because it indicates that very narrow lines can be written into the resist and subsequently metalated even if all of the organic material is not removed from the pattern: in this case we believe that Cu nucleates in exposed regions and then the nuclei grow together to form the line. At the present time we are unable to determine the conductivity of the lines. Figure 2b emphasizes the dense Cu surface morphology and the well-defined edges of the pattern (lower right part of the figure).

Figure 3 shows the results obtained when a nominally 5 x 5 µm

Figure 3

STM-patterned feature, which was created using only 2 STM scans at +8 V bias, is exposed to (hfac)Cu(1,5-COD) for 15 min at 120 °C. Three important observations result from this micrograph. First, the metalated part of the pattern is not square, and the long axis of the rectangular metal feature is parallel to the fast-scan direction of the STM. Second, Cu does not deposit homogeneously

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but instead nucleates along the fast-scan direction. Third, a significant number of Cu nuclei are present outside the patterned area. From these results we conclude that the bottom of the etched feature is not completely free of organic material, and that Cu preferentially nucleates and grows from those regions of the substrate that are cleanest. The presence of Cu islands outside the patterned region suggest thermal degradation of the resist upon extended exposure to (hfac)Cu(1,5-COD), which is consistent with the results of the control experiments discussed earlier.

To summarize, we have reported two important results. First, methyl-terminated, self-assembled monolayers passivate Au surfaces towards (hfac)Cu(1,5-COD) disproportionation and therefore substrate metalization. Second, STM lithography can be used to pattern monolayer resists, which can be metalized subsequently using low-temperature Cu CVD methods. This strongly suggests that the lithographic step removes, or sufficiently disrupts, the resist so that the (hfac)Cu(1,5-COD) precursor is able to interact with the catalytically active Au surface. It appears that more complete removal of the n-alkanethiol monolayer results in a more dense morphological structure of the Cu deposits and that lower temperatures and shorter exposure times for metalization enhance selectivity. We are presently refining both the lithographic and CVD aspects of this work, and the results of those experiments will be reported in the near future.

Acknowledgments

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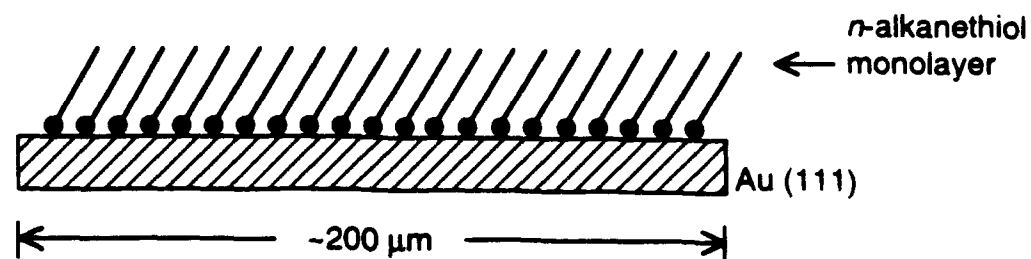27. Rabe, J. P.; Buchholz, S. *Appl. Phys. Lett.* **1991**, *58*, 702.

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44. We found that STM or SEM imaging of the STM-patterned resists prior to CVD severely degrades the passivating function of the monolayer. Therefore, we are unable to present micrographs of exactly the same pattern before and after Cu CVD.
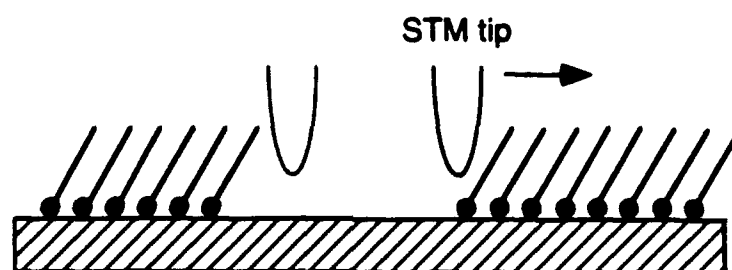
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Figure Captions

1. (a) SEM micrograph of 5 STM-patterned regions of a monolayer resist prior to Cu deposition. The square patterns are 0.1, 0.5, 1.0, 2.0, and 5.0 μm on a side, and they were fabricated using the following STM conditions: 0.1 μm, 4 scans at +4 V bias and 8 Hz followed by 4 additional scans at +0.3 V and 8 Hz; 0.5 μm, 4 scans at +6 V bias and 4 Hz followed by 4 additional scans at +0.3 V and 8 Hz; 1.0 - 5.0 μm, 4 scans at +8 V bias and 2 Hz followed by 4 additional scans at +0.3 V and 4 Hz. The tip current was always 0.15 nA. (b) SEM micrograph of an analogous STM-patterned monolayer after Cu CVD at 120 °C for 3.5 min. Patterns were formed using the same conditions listed for (a). Three metalated rectangular features (lower left part of the micrograph) are also shown.

2. High resolution SEM micrographs of two Cu patterns. (a) shows that the 50-nm wide Cu line in Figure 1b is continuous and (b) emphasizes the dense Cu-surface morphology and sharp pattern definition (lower right).

3. SEM micrograph of an incompletely etched 5 x 5 μm (nominal) STM-defined pattern following Cu metalization. The pattern was created by scanning the STM twice at +8 V bias (0.11 nA, 1.34 Hz).
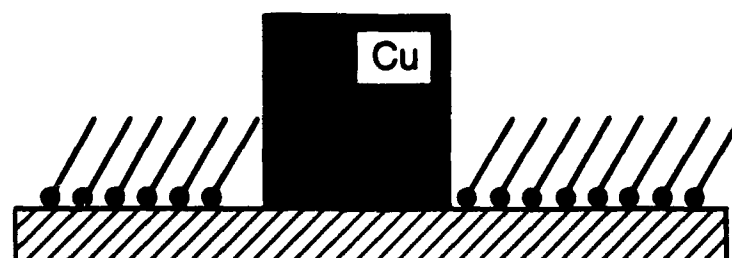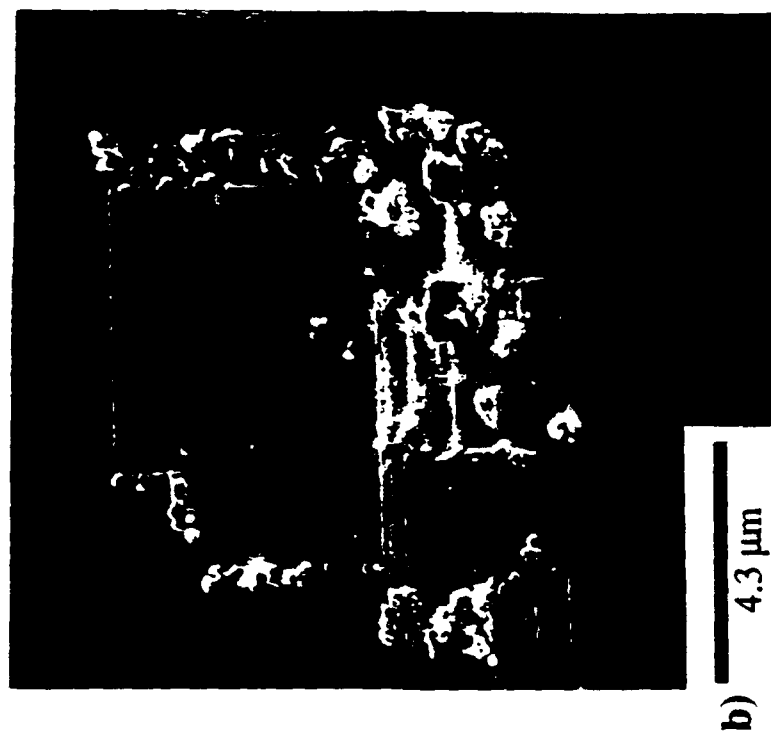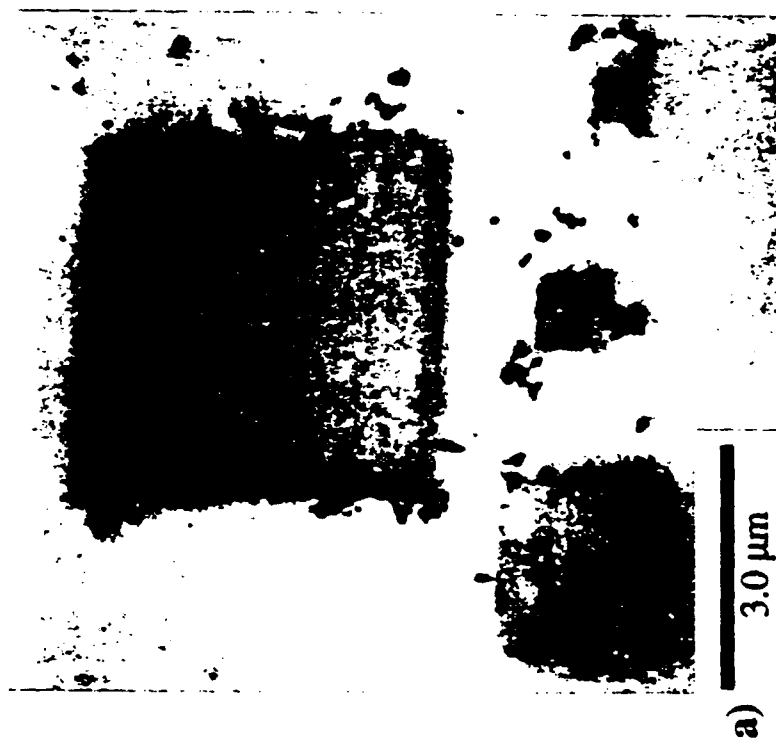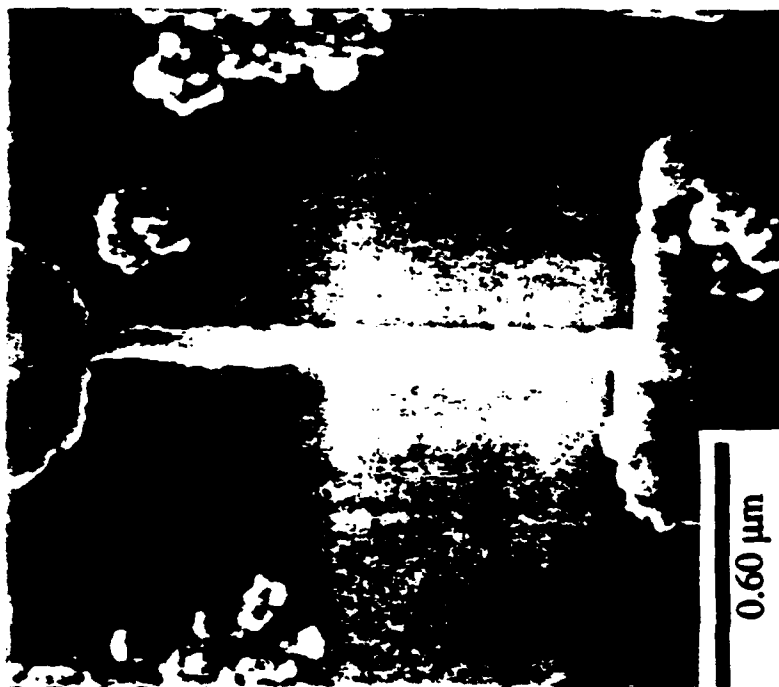
Substrate Modification

n-alkanethiol
monolayer

|← ~200 μm →|

Au (111)

STM Lithography

STM tip

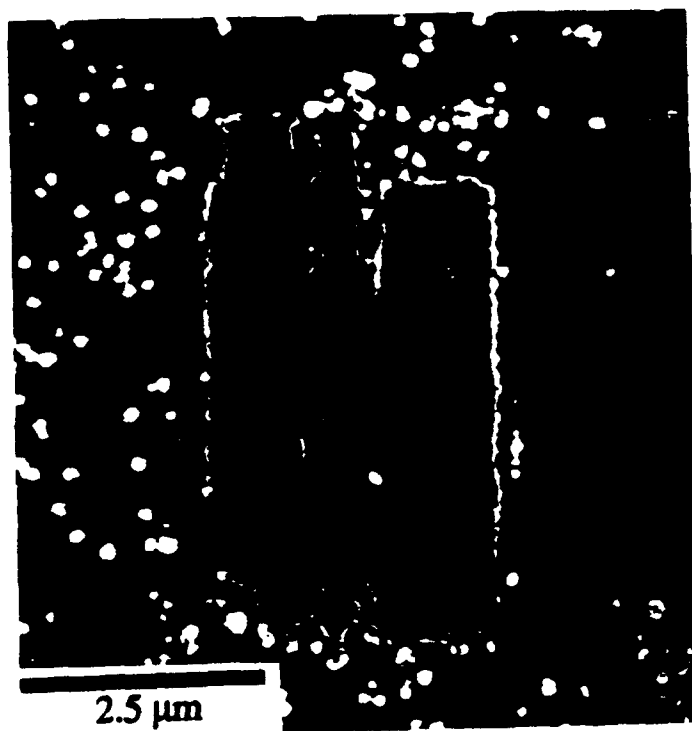## Chemical Vapor Deposition

Cu

Scheme I / Corbitt et. al.

b) 4.3 μm

a) 3.0 μm

a)

b)

1.00 μm

0.60 μm

2.5 μm

Figure 3 / Corbin et al.